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13. ABSTRACT (Maximum 200 words)

Research performed over the period April 1, 2001 – September 30, 2002 supported by the U.S. Army Research Office (Grant number: DAAD19-00-1-0064) is described. This research program is concerned with the development of theoretical methods and computer codes for simulating fundamental processes in energetic materials. The work is being carried out in collaboration with Dr. Betsy M. Rice at ARL. The work during this report period focused on the following: The development and demonstration of methods and computer codes for calculating rates of physical and chemical processes in many-atom systems by Monte Carlo variational transition-state theory. Specifically, we demonstrated the methods and codes by calculating rates of atomic diffusion on metal surfaces for comparison with data in the literature.

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SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS:

Predicting Trends in Rate Parameters for Self-Diffusion on FCC Metal Surfaces

We have carried a comprehensive study of the fundamental aspects of self-diffusion on metal surfaces. A manuscript has been accepted for publication in Surface Science. The following is a brief description of the work.

Dynamically corrected Monte Carlo variational transition-state theory (MCVTST) (See, e.g., L. M. Raff, I. NoorBatcha, D. L. Thompson, J. Chem. Phys. **85** 3081 (1986).] with Lennard-Jones potentials have been used to study hopping self diffusion on the (100), (111), and (110) surfaces of nine FCC metals: Ag, Al, Au, Cu, Ir, Ni, Pd, Pt, and Rh. The potential parameters were determined from the known experimental values of cohesive energies and lattice constants.

For the (100) surfaces the computed values of R , the ratio of the cohesive energy to the activation energy, are in accord with the *ab initio* generalized gradient approximation results of Feibelman [P. J. Feibelman, Surf. Sci. **423** 169 (1999).]: $R=6$ for these nine metals. The value of R is found to be 30 for the (111) surfaces. For the hopping diffusion on the (110) surface, R depends on the direction of diffusion: R is 5 and 2.8 along the $[1\bar{1}0]$ and $[001]$ directions, respectively. As pointed out by Feibelman this knowledge of the value of R for a given kind of the surface can be useful as a standard to assess whether a measured or computed activation energy value is unusual.

For given Miller indices of the surface and the direction of the diffusive channel the pre-exponential factor, D_0 , for all these metals is found to vary within a factor of three from $(D_0)_{av}$, the average of the D_0 of all the nine elements studied. $(D_0)_{av}$ is found to depend on R and the distance between the neighboring binding sites according to a simple empirical relationship. Similarly, the reduced pre-exponential factor, D_0^* , can also be expressed in terms of R , lattice constants, and the distance between the two nearest binding sites. This value of $(D_0)_{av}$ or D_0^* can be useful in extracting the activation energy from limited experimental data and the Arrhenius equation.

A paper has been published; the abstract follows:

Abstract [Paras M. Agrawal, Betsy M. Rice, and Donald L. Thompson, "Predicting Trends in Rate Parameters for Self-Diffusion on FCC Metal Surfaces" Surface Science **515**, 21-35 (2002).] The hopping self diffusion coefficient of an adatom on the (100), (110) and (111) surfaces of nine FCC metals have been investigated using Monte Carlo variational transition state theory and the Lennard-Jones (L-J) interactions. The metals that have been studied are Ag, Al, Au, Cu, Ir, Ni, Pd, Pt, and Rh. The potential parameters for the L-J interactions have been determined from the known experimental values of cohesive energies and lattice constants. The ratio, R , of the cohesive energy to the activation energy for diffusive hopping on the (111) and (100) surfaces are found to be 30 and 6, respectively. For diffusive hopping on the (110) surface, R depends on the direction of diffusion: R is 5 and 2.8 along the $[1\bar{1}0]$ and $[001]$ directions, respectively. The pre-exponential factor, D_0 , for these metals is found to vary within a factor of three from the corresponding average value, $(D_0)_{av}$ for a given surface and diffusion channel. Also, the pre-exponential factors corresponding to diffusion on the (111), (100), (110) $[1\bar{1}0]$ and (110) $[001]$ surfaces are found to satisfy an empirical expression in terms of R , lattice constant, and the distance between the two nearest binding sites. The results on the activation energies and pre-exponential factors are compared with other experimental and theoretical data.

Predicting Melting Points

Molecular dynamics simulations at constant pressure and number of particles have been performed to study the melting of argon. The temperature was varied at the rate of 0.001 K per integration time step to simulate heating. The system was described by exp-6 and Lennard-Jones interaction potentials. The perfect lattice as well as lattices with voids was investigated. The conversion of crystalline Ar into liquid was monitored by observing the sudden drop in the translational-order parameter and the density and the sudden increase in the energy per atom.

Thermodynamic melting point data based on the exp-6 potential are available in the literature over the pressure range 0.081 to 531.6 kbar. Our computed value for the melting point of the perfect Ar lattice is about 15% higher than the thermodynamic melting point. The predicted melting point of perfect crystals is unrealistically high. As Solca *et al.* [Chem. Phys. **224**, 253, (1997)] have pointed out, the "true" melting point is obtained by simulating solids with voids. As the void size increases the melting point decreases until a "critical" void size is reached where the melting point levels off. The melting point in the plateau region is in good agreement with the thermodynamic melting point, which we take to be the true value for this potential.

We have studied solids with a single void of various sizes and the effect on the melting point of distributing various size voids throughout the solid. This study has provided better understanding of the fundamental effects of voids in solids on the phase transition as well as the most efficient way of selecting initial conditions for simulating melting. A manuscript is being prepared for publication.

PUBLICATIONS, REPORTS, AND THESES

Manuscripts submitted and published:

Paras M. Agrawal, Betsy M. Rice, and Donald L. Thompson,
"Predicting Trends in Rate Parameters for Self-Diffusion on FCC Metal Surfaces"
Surface Science **515**, 21-35 (2002).

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None